PATENT COOPERATION T...ATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
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in its capacity as elected Office

Date of mailing (day/month/year) 20 July 2000 (20.07.00)	
International application No. PCT/GB99/04081	**Applicant's or agent's file reference** PFC 1417 PCT
International filing date (day/month/year) 09 December 1999 (09.12.99)	**Priority date** (day/month/year) 09 December 1998 (09.12.98)
Applicant COOPER, Susan, Joy et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

10 June 2000 (10.06.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was [ ] was not made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38

09/857759

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

WISHART, Ian C.
JOHNSON MATTHEY TECHNOLOGY CENTRE
Blounts Court
Sonning Common
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GRANDE BRETAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	15.03.2001
Applicant's or agent's file reference PFC 1417 PCT	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB99/04081	09/12/1999	09/12/1998

Applicant
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

   The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

   Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

   For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Myers, J Tel.+49 89 2399-8111

Form PCT/IPEA/416 (July 1992)

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REC'D 20 MAR 2001

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PFC 1417 PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB99/04081	International filing date *(day/month/year)* 09/12/1999	Priority date *(day/month/year)* 09/12/1998
International Patent Classification (IPC) or national classification and IPC H01M4/92		
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand 10/06/2000	Date of completion of this report 15.03.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Del Piero, G Telephone No. +49 89 2399 8579

Form PCT/IPEA/409 (cover sheet) (January 1994)

7.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/04081

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

Description, pages:

1-29	as originally filed	

Claims, No.:

1-11,16	with telefax of	24/01/2001

Drawings, sheets:

1/5-5/5	as originally filed	

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

   ☐ the entire international application.

   ☒ claims Nos. 16.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 16 are so unclear that no meaningful opinion could be formed (*specify*):
see separate sheet

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination report cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

   ☐ the written form has not been furnished or does not comply with the standard.

   ☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

   Novelty (N) Yes: Claims 1-11

	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-9, 11
	No:	Claims	10
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
   see separate sheet

III.

Claim 16 is vague and indeterminate in scope (it cannot be put in a definite category) to such an extent that no assessment as to whether its subject-matter meets the requirements of novelty, inventive step and industrial applicability is possible.

Moreover, this claim is contrary to the provisions of R.6.2(a).

V.

Novelty.

The subject-matter of present claims 1-11 is neither disclosed in nor fairly derivable from the available prior art.

In particular, it is distinguished from the closest state of the art as represented by the acknowledged EP-A-0 838 872 on the basis of the presence of a second catalytic component.

Inventive step.

An inventive step can be acknowldeged to the subject-matter of claims 1-9 and 11 on the basis of the improved CO tolerance of the electrode, which is demonstrated for a number of catalyst compositions contemplated by claim 1.

This, however, does not apply to the subject-matter of claim 10, which is too broad in scope in that it covers an exceedingly high number of possible compositions of the first and second catalytic components which is not justified by the limited number of

compositions for which a technical effect supporting an inventive step has been shown in the description.

1. An electrode structure comprising a first catalytic component and a second catalytic component, wherein:

   (a) said first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y, wherein Y is Mo, W or an oxide of Mo or W, and optionally a third metal component X which is alloyed with the platinum and which is one or metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; and

   (b) said second catalytic component comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum and is one or more metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; and

   wherein the first and second catalytic components are in ionic contact with each other.

2. An electrode structure according to claim 1 wherein X is selected from Ru, Mn, Co, Ni, Rh and Ni.

3. An electrode structure according to claim 1 or claim 2, wherein M is selected from Ru or Rh.

4. An electrode structure according to claim 1, wherein the first catalytic component is selected from: Pt/Mo, Pt/Mo/Co, Pt/W/Co, Pt/Ru/WO_3 and Pt/Ti/W; and the second catalytic component is Pt/Ru.

5. An electrode comprising an electrode structure according to any preceding claim wherein the electrocatalyst materials are present on one side of a gas diffusion material.

6. A catalysed membrane comprising an electrode structure according to any one or more of claims 1 to 4 wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material.

7. An MEA comprising an electrode structure according to any one or more of claims 1 to 4.

8. An electrode according to claim 5, a catalysed membrane according to claim 6 or an MEA according to claim 7 wherein the two catalyst materials are formulated into two separate layers.

9. An electrode according to claim 5, a catalysed membrane according to claim 6 or an MEA according to claim 7 wherein the two catalyst materials are formulated into one mixed layer.

10. A fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the

platinum.

11. Use of an electrode structure according to any one or more of claims 1 to 8 in a fuel cell.

16. An electrode, such as an anode, such as a fuel cell anode; an electrochemical device, such as an MEA; a use; or a method, substantially as hereinbefore described with particular reference to the examples.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

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(54) Title: ELECTRODE STRUCTURE

(57) Abstract

A piston tolerant anode structure for use in fuel cells, in particular suitable for use on proton exchange membrane fuel cells, comprising a first catalytic component Pt–Y where Y is a bronze forming element, and optionally a third metal x alloyed with the platinum, and a second catalytic component It–M where M, metal, is alloyed with the platinum. An anode, a catalysed membrane, a membrane electrode assembly and a fuel cell comprising said electrode structure, are disclosed.

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ELECTRODE STRUCTURE

The invention relates to an improved electrode structure and specifically to a poison-tolerant anode structure for fuel cells, suitable for use in particular in proton exchange membrane fuel cells. The invention further relates to an anode, a catalysed membrane, a membrane electrode assembly and a fuel cell comprising said electrode structure.

Electrochemical cells invariably comprise at their fundamental level a solid or liquid electrolyte and two electrodes, the anode and cathode, at which the desired electrochemical reactions take place. A fuel cell is an energy conversion device that efficiently converts the stored energy of its fuel into electrical energy by combining hydrogen, stored as a gas, or methanol, stored as a liquid or gas, with oxygen to generate electrical power. The hydrogen or methanol is oxidised at the anode and oxygen reduced at the cathode. In these cells gaseous reactants and/or products have to be diffused into and/or out of the cell electrode structures. The electrodes therefore are specifically designed to be porous to gas diffusion in order to optimise the contact between the reactants and the reaction sites in the electrode to maximise the reaction rate. An electrolyte is required which is in contact with both electrodes and which may be alkaline or acidic, liquid or solid. In a solid polymer fuel cell (SPFC), also known as a proton-exchange membrane fuel cell (PEMFC), the electrolyte is a solid proton-conducting polymer membrane, commonly based on perfluorosulphonic acid materials. These electrolytes must be maintained in a hydrated form during operation in order to prevent loss of ionic conduction through the electrolyte; this limits the operating temperature of the PEMFC to between 70°C and 120°C, depending on the operating pressure. The PEMFC does, however, provide much higher power density output than

the other fuel cell types, and can operate efficiently at much lower temperatures. Because of this, it is envisaged that the PEMFC will find use in vehicular power generation and small-scale residential power generation applications. In particular, vehicle zero-emission regulations have been passed in areas of the United States that are likely to restrict the use of the combustion engine in the future. Pre-commercial PEMFC-powered buses and prototype PEMFC-powered vehicles are now being demonstrated for these applications.

Due to the relatively low operating temperatures of these systems, the oxidation and reduction reactions require the use of catalysts in order to proceed at useful rates. Catalysts, which promote the rates of electrochemical reactions, such as oxygen reduction and hydrogen oxidation in a fuel cell, are often referred to as electrocatalysts. Precious metals, in particular platinum, have been found to be the most efficient and stable electrocatalysts for all low-temperature fuel cells operating below 300°C. The platinum electrocatalyst is provided as very small particles (~20-50Å) of high surface area, which are often, but not always, distributed on and supported by larger macroscopic conducting carbon particles to provide a desired catalyst loading. Conducting carbons are the preferred materials to support the catalyst.

In the PEMFC the combined laminate unit formed from the membrane and the two electrodes is known as a membrane electrode assembly (MEA). The MEA will typically comprise several layers, but can in general be considered, at its basic level, to have five layers, which are defined principally by their function. On either side of the membrane an anode and cathode electrocatalyst is incorporated to increase the rates of

the desired electrode reactions. In contact with the electrocatalyst containing layers, on the opposite face to that in contact with the membrane, are the anode and cathode gas diffusion substrate layers. The anode gas diffusion substrate is designed to be porous and to allow the reactant hydrogen or methanol to enter from the face of the substrate exposed to the reactant fuel supply, and then to diffuse through the thickness of the substrate to the layer which contains the electrocatalyst, usually platinum metal based, to maximise the electrochemical oxidation of hydrogen or methanol. The anode electrocatalyst layer is also designed to comprise some level of the proton conducting electrolyte in contact with the same electrocatalyst reaction sites. With acidic electrolyte types the product of the anode reaction are protons and these can then be efficiently transported from the anode reaction sites through the electrolyte to the cathode layers. The cathode is also designed to be porous and to allow oxygen or air to enter the substrate and diffuse through to the electrocatalyst layer reaction sites. The cathode electrocatalyst combines the protons with oxygen to produce water. Product water then has to diffuse out of the cathode structure. The structure of the cathode has to be designed such that it enables the efficient removal of the product water. If water builds up in the cathode, it becomes more difficult for the reactant oxygen to diffuse to the reaction sites, and thus the performance of the fuel cell decreases. In the case of methanol fuelled PEMFCs, additional water is present due to the water contained in the methanol, which can be transported through the membrane from the anode to the cathode side. The increased quantity of water at the cathode requires removal. However, it is also the case with proton exchange membrane electrolytes, that if too much water is removed from the cathode structure, the membrane can dry out and the performance of the fuel cell also decreases.

The complete MEA can be constructed by several methods. The electrocatalyst layers can be bonded to one surface of the gas diffusion substrates to form what is known as a gas diffusion electrode, which can be either an anode or a cathode. The MEA is then formed by combining two gas diffusion electrodes with the solid proton-conducting membrane. Alternatively, the MEA may be formed from two porous gas diffusion substrates and a solid proton-conducting polymer membrane which has been catalysed on both sides; or indeed the MEA may be formed from one gas diffusion electrode and one gas diffusion substrate and a solid proton-conducting polymer catalysed on the side facing the gas diffusion substrate.

Electrodes, catalysed membranes or MEA's are employed in many different electrochemical devices in addition to fuel cells, including metal-air batteries, electrochemical gas sensors, and electrochemical reactors for the electrosynthesis of useful chemical compounds.

In most practical fuel cell systems, the hydrogen fuel is produced by converting a hydrocarbon-based fuel (such as methane) or an oxygenated hydrocarbon fuel (such as methanol) to hydrogen in a process known as reforming. This fuel, referred to as reformate, contains (in addition to hydrogen) high levels of carbon dioxide (CO_2), of around 25%, and small amounts of impurities such as carbon monoxide (CO), typically at levels of around 1%. For fuel cells operating at temperatures below 200°C, and especially for the PEMFC operating at temperatures around 100°C, it is well known that CO, even at levels of 1-10ppm, is a severe poison for the platinum electrocatalysts

present in the electrodes. This leads to a significant reduction in fuel cell performance, *ie* the cell voltage at a given current density is reduced. This deleterious effect is more pronounced in PEMFCs operating at lower temperatures. In addition, it has been found that the CO_2 present in the fuel stream can also cause a loss of performance. This performance decay is usually small compared to the effect of CO.

Various methods have been employed to alleviate anode CO poisoning. For example, reformer technology has been redesigned to include an additional catalytic reactor, known as a preferential or selective oxidation reactor. This involves the injection of air or oxygen into the hydrogen-containing reactant gas stream, prior to it passing over the selective oxidation catalyst, to oxidise the CO to CO_2. This can reduce the levels of CO from 1-2% down to below 100ppm. However, even at these levels, the anode electrocatalyst in the PEMFC is still poisoned.

It has also been found that poisoning of the electrocatalyst by CO at levels of 1-100ppm can be reduced by the use of an oxygen or air bleed directly into the anode gas stream just before it enters the anode chamber of the fuel cell itself. This is described by Gottesfeld and Pafford in J. Electrochem. Soc., 135, 2651 *et seq* (1988). This technique is believed to have the effect of oxidising the residual CO in the fuel to CO_2, the reaction being catalysed by electrocatalyst sites present in the anode:

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

This technique provides fuel cell performance that is much closer to the performance

observed when no CO is present in the fuel stream. However, the air bleed technique does not usually improve the deleterious effects of CO_2 on performance and there are concerns over the long-term sustainability of the cell performance when this approach is employed. This is particularly the case if high levels of air bleed, equivalent to 4% and above of the total reformate fuel volume, are required.

However, the preferred technique for alleviating fuel cell performance reduction due to anode CO poisoning is to employ an anode electrocatalyst that is itself more poison-tolerant, but which still functions as a hydrogen oxidation catalyst in the present of CO. As described by, for example, Niedrach *et al* in Electrochem. Technol., 5, 318, (1967), the use of a bimetallic anode electrocatalyst comprising platinum/ruthenium, rather than the more conventionally-used mono-metallic platinum-only electrocatalyst, shows a reduction in the poisoning effect of the CO at typical PEMFC operating temperatures. However, again, it was not possible fully to attain the performance observed on pure hydrogen, *ie* in the absence of CO in the fuel stream, by using this approach in isolation.

There have been a number of attempts to improve the performance of anode electrocatalysts operating in the presence of hydrogen fuels containing CO. These have taken the approach of modifying existing state-of-the-art catalysts, such as combining platinum/ruthenium with other components. In 1995, Chen *et al* (J. Electrochem. Soc., 142, (10)) discussed the need to develop CO-tolerant catalysts and studied the oxidation of impure H_2 on Teflon®-bonded carbon-supported platinum/ruthenium/ tungsten oxide electrodes. The use of tungsten oxide (WO_3) as a

promoter of improved activity of platinum catalysts towards impure H_2 was not new. As far back as 1965, it was known that tungsten oxides were effective in promoting the electro-oxidation of CO on platinum-containing electrodes in acid-electrolyte fuel cells (Niedrach and Weinstock, Electrochem. Technol., 3, 270-5 (1965)). A more recent example of a catalyst having improved CO tolerance is given in European patent specification no. EPA 838 872.

EPA 838 872 relates to a ternary catalyst comprising Pt-M-Y, wherein Pt-M is an alloy of platinum and one or more metals selected from the transition metal elements or from Groups IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press, and Y is a bronze forming element or an oxide thereof, characterised in that the Pt-M alloy is in intimate contact with Y, and provided that M is not Ru if Y is WO_3.

However, such electrocatalysts aimed at improving CO tolerance apparently do not also have the effect of improving performance when CO_2 is present in the reformate fuel. Hence, for example, in the case of certain materials described in EPA 838 872, improved CO tolerance is observed, but at the same time the presence of CO_2 in the reformate stream causes larger performance losses than those observed with state-of-the-art alloys of platinum and ruthenium. This behaviour is most likely due to the CO tolerance mechanism for the catalysts described in EPA 838 872 differing from that observed with Pt/Ru alloys.

We have now surprisingly found that significant improvement in both CO and CO_2

tolerance can be achieved by providing an electrode structure in which the state-of-the-art Pt/Ru-type electrocatalyst is functionally linked with a further electrocatalyst. This has never before been achieved.

An anode structure of the present invention when used in a PEMFC shows improved tolerance to both CO and CO_2 poisons whilst maintaining high activity for the desired electrochemical reaction, and is therefore of use in fuel cells which use an impure feed. The anode structure may be of benefit in both phosphoric acid and solid polymer fuel cells. Specifically, it shows tolerance to both CO and CO_2 poisons in reformate fuel. The anode structure may also be of benefit in these fuel cells when the fuel is methanol.

Accordingly, the present invention provides an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M where M is a metal alloyed with the platinum.

The term "functionally linked" in the context of the present invention means that both materials are in ionic contact with each other. This may be achieved by adding an ion conducting material to each of the catalysts when they are formulated into the electrode structure of the invention. In the case of an anode structure for a PEMFC, the ion conducting material is a proton conducting material, which can be the same as that

employed as the polymeric electrolyte membrane of the MEA.

The Pt-M or Pt-X alloy is preferably more than a mere physical mixture of Pt with metal(s), since the platinum and metal(s) are preferably heat-treated to promote a measurable interaction between the platinum and metal(s) to change the intrinsic properties of the platinum metal. Heat-treatment causes a significant number of atoms of the metal(s) to be incorporated into the atomic crystal lattice, or unit cell, of the platinum particle. This process usually distorts the dimensions of the platinum unit cell, since the atoms of the metal(s) will generally be of a different size from those of the platinum, and this can usually be measured by techniques such as X-ray diffraction. The characteristic dimensions of the platinum unit cell, referred to by crystallographers as the lattice parameter, can be shown to have altered due to the fact that two or more metals, with different atomic sizes, have been incorporated into a single, homogeneous metal alloy particle at the atomic level.

Preferably, the one or more metals(s) X or M, when present, is or are selected from the groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press; for example, X metals can be from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr, Hf and Sn; especially Ru, Mn, Ti, Co, Ni and Rh and M metals can be from the same group especially Ru and Rh.

Component Y may either be alloyed with the Pt-X alloy (the resulting alloy being as defined hereinbefore) or may be unalloyed but in physical contact with the alloy.

Component Y may be a bronze-forming element or an oxide thereof. A 'bronze' material is defined by Wold and Dwight in Solid State Chemistry - Synthesis, Structure, and Properties of Selected Oxides and Sulfides, Chapman & Hall as " . . . an oxide with intense colour (or black), having a metallic lustre and showing either semi-conducting or metallic behaviour. A principle characteristic of bronzes is their range of composition, which results in the transition metal exhibiting a variable formal valence." Suitable bronzes include non-stoichiometric alloys of the transition metal with hydrogen.

The component Y is suitably selected from one or more of the Group IVB to VIB elements and rhenium or an oxide thereof, for example Ti, V, Nb, Ta, Mo, W, Re, or an oxide thereof; suitably Ti, V, Ta, Mo, W, or an oxide thereof; preferably Mo or W, or an oxide thereof.

Preferably, the second catalytic component is one wherein the Pt-M is Pt (alone) or an alloy (as defined) of Pt/Ru.

The term "electrode structure" in the context of the present invention means the specific compositional aspects of those parts of the electrochemical cell at which the electrochemical reactions take place. It does not specifically refer to any particular physical embodiment of the invention. The physical embodiments of the invention can take several forms. The electrocatalyst materials can be applied to one side of a gas diffusion substrate material to produce an electrode, which can be either an anode or cathode, comprising the electrode structure of the invention.

Thus in a further aspect, the present invention provides an electrode comprising an electrode structure of the present invention wherein the electrocatalyst materials are present on one side of a gas diffusion substrate material.

Alternatively the electrocatalyst materials can be applied to one side of the polymer electrolyte membrane material to produce a catalysed membrane, comprising the electrode structure of the invention.

Thus in a further aspect the present invention provides a catalysed membrane comprising an electrode structure according to the present invention wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material..

An MEA for use in, for example, a PEMFC, as herein described is a five layer unit, comprising a polymer electrolyte membrane in the centre, with an electrocatalyst containing layer either side of the membrane and a gas diffusion substrate layer in contact with the electrocatalyst containing layers on the opposite face of the layer to that in contact with the membrane. An MEA comprising the electrode structure of the invention, can be formed from electrodes as defined above, by bonding two electrodes, at least one of which comprises the electrode structure of the invention, either side of a polymer electrolyte membrane. Alternatively the MEA may be formed from the catalysed membrane by applying gas diffusion substrate materials either side of a

catalysed membrane, in which at least one catalysed side of the membrane comprises the electrode structure of the invention.

Thus in a further aspect, the present invention provides an MEA comprising an electrode structure according to the present invention.

In the above aspects of the present invention namely when formed into electrodes, catalysed membranes or an MEA from either of these two components, the two catalyst materials can be formulated into two separate layers which are applied to one side of either the gas diffusion substrate material or to the polymer electrolyte membrane, but in which they are still functionally linked. It is also possible that the two catalyst materials may be mixed together and formed into one layer containing both catalysts and applied to one side of either the gas diffusion substrate material or the polymer electrolyte membrane.

An electrode comprising the electrode structure of the invention may be formed wherein each catalyst is formulated into a separate layer in which a first layer comprising the first catalyst material, as herein defined, is in contact with one side of the gas diffusion substrate material, and a second layer comprising the second catalyst material is in contact with the opposite face of the first catalyst layer to that in contact with the gas diffusion substrate. Alternatively a catalysed membrane comprising the electrode structure of the invention may be formed wherein each catalyst is formulated into a separate layer in which a first layer comprising the second catalyst material, as herein defined, is in contact with one side of the polymer electrolyte membrane

material, and the second layer comprising the first catalyst material is in contact with the opposite face of the second catalyst layer to that in contact with the polymer electrolyte membrane.

In a further aspect, the present invention provides a fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum.

In a final aspect, the present invention provides the use of an electrode structure according to the present invention in a fuel cell.

The invention will now be described further with reference to the following Examples and drawings in which:

Figure 1: shows fuel cell performance data of cell voltage vs time for operation of two PtRu (thick line and line with ●), PtRuW (line with ■), PtTiW (line with ✕) and PtCoMo (line with ▲) catalysts in a gas stream containing 100ppm CO in hydrogen. The anode platinum loadings are respectively 0.37, 0.25, 0.29, 0.45 and 0.29 mg Pt/cm^2.

Figure 2 : shows fuel cell performance data of cell voltage *vs* time for operation of the two PtRu (thick line and line with ●), PtRuW (line with ■), PtTiW (line with ×) and PtCoMo (line with ▲) catalysts in a gas stream containing 25% CO_2 and 75% hydrogen. The anode platinum loadings are the same as in Figure 1.

Figure 3 presents single cell performance data for electrode bilayers according to the invention operating in 25% CO_2 and 75% hydrogen. The bilayers comprise of catalyst layers of PtTiW (line with ×) , PtRuW (line with ■), PtCoMo (line with ▲) and PtCoW (dashed line) containing 0.16, 0.12, 0.26 and 0.27 mg Pt cm^{-2} and layers of PtRu catalyst at loadings of 0.13, 0.25, 0.14 and 0.24 mg Pt cm^{-2}, respectively. Figure 3 also shows the comparative example PtRu (thick line) which is also presented in Figure 1.

Figure 4 shows that, at the same time, the performance of the bilayer electrodes of the invention in hydrogen containing 100 ppm CO is significantly improved over the comparative PtRu sample performance decay, while the total platinum loading in both layers is very similar in all cases.

Figure 5 shows the single cell performances of two MEA's, one an electrode bilayer according to the invention, and the other a single catalyst layer, operating on gas mixtures of CO and CO_2 in hydrogen, which has been used to simulate reformate gas compositions. The MEA's have been tested on two different gas mixtures; 40ppm CO and 25% CO_2 in hydrogen (closed symbols), and 100ppm CO and 25% CO_2 in hydrogen (open symbols). The bilayer

comprises of a catalyst layer of PtCoMo at loadings of 0.15 mg Pt/cm^2 and a layer of a PtRu catalyst at a loading of 0.31 mg Pt/cm^2 (lines with squares). The single layer electrode comprised of the same PtRu catalyst at a loading of 0.29 mg Pt/cm^2 (lines with circles).

COMPARATIVE EXAMPLE 1

A catalyst containing platinum and ruthenium at 41.80 wt% Pt and 20.78wt% Ru supported on Cabot Vulcan XC72R carbon, was prepared using a process comprising the deposition of Pt onto the conductive carbon black substrate by the hydrolysis of an aqueous solution of chloroplatinic acid and ruthenium trichloride by a solution of sodium hydrogen carbonate in the presence of the carbon black, as disclosed in EP 450 849. The catalyst was reduced using aqueous formaldehyde solution, filtered, washed free of soluble chloride salts and dried at 100°C. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicating significant alloying of the Ru with the Pt. From this catalyst, a catalyst ink was prepared and a fuel cell anode was printed onto pre-teflonated Toray TPG90 paper. Inks and electrodes are prepared as detailed in Example 2 of European patent specification no. EPA 731 520. The platinum loading of this electrode was $0.37 mgPt/cm^2$.

COMPARATIVE EXAMPLE 2

A catalyst containing platinum and ruthenium at 19.2 wt% Pt and 9.3 wt% Ru

supported on Cabot Vulcan XC72R carbon, was prepared using the process as described in Comparative Example 1 and as disclosed in EP 450 849. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.88X, indicating significant alloying of the Ru with the Pt. An Electrode was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.25mgPt/cm^2.

COMPARATIVE EXAMPLE 3

A catalyst containing platinum, ruthenium and tungsten at 16.65wt%Pt, 8.32wt%Ru and 10.77wt% W was prepared. A PtRu catalyst (7.5g), as described in Comparative Example 2, was slurried in 1 litre of demineralised water for one hour. A 1 wt% solution of sodium tungstate in demineralised water was prepared containing 1.98g tungsten. This solution was converted to tungstic acid by passing it through an exchange column, comprising Dowex 50-X8 ion-exchange resin, and fed directly into the slurry. The resultant catalyst was stirred overnight and then filtered, dried at 105°C in air and fired at 500°C in a gas mixture containing 6%CO in CO_2. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicting significant alloying of the Ru with the Pt, together with the presence of crystalline WO_3. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.29mgPt/cm^2.

COMPARATIVE EXAMPLE 4

A catalyst containing Pt, Ti and W at 34.41 wt% Pt, 2.02wt% Ti and 10.63wt% W was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (16g) in a 6 litre solution of potassium hydrogen carbonate (25g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 8g Pt). The resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was dried at 100°C in air. The catalyst was re-slurried in a litre solution of potassium hydrogen carbonate (2.5g) and heated till under reflux. A 2wt% solution of titanium trichloride (containing 0.45g Ti) and urea (3.39g) was added dropwise. The ratio of alkali to metal salts for both steps was such as to ensure complete hydrolysis and precipitation of the metal hydrous oxides/hydroxides onto the carbon.

The slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The wet cake was then dispersed in a litre of demineralised water. To this slurry was added dropwise a 1wt% solution of tungsten (2.32g) in water. This was prepared by the dissolution of tungsten powder in hydrogen peroxide solution, followed by decomposition of the excess peroxide by platinum black. The combined slurry was then evaporated to dryness. The resulting catalyst was then heated at 650°C in flowing 5% hydrogen in nitrogen for 1 hour. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.93X, which indicated little alloying of the components. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.45mgPt/cm^2.

COMPARATIVE EXAMPLE 5

A catalyst containing Pt, Co and Mo at 21.0wt% Pt, 0.2wt% Co and 1.0wt% Mo was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (94.5g) in a 6 litre solution of sodium hydrogen carbonate (67.4g) under reflux, was added first a 2wt% solution of chloroplatinic acid (containing 24.2g Pt), followed by a 2wt% solution of cobalt dichloride (containing 1.7g Co). The amount of sodium hydrogen carbonate was calculated to be sufficient to just precipitate both Pt and Co as their hydrous oxides/hydroxides. The resulting catalyst was filtered, washed with demineralised H_2O until chloride free and dried at 100°C. A portion of the dried catalyst (21.8g) was reslurried in 1.5 litres of demineralised H_2O and stirred. To this was added disodium molybdate dihydrate (1.7g) and the slurry stirred until complete dissolution. To the resulting slurry was added a solution of 1,8-hydroxyquinoline (1.0g) in 40 cm^3 of ethanol. The amount of 1,8-hydroxyquinoline added being 2 molar equivalents of the amount of Mo added. The slurry was heated until under reflux and the pH adjusted to 4 by the addition of acetic acid. The slurry was boiled for 60 minutes to remove the ethanol, after which the slurry was cooled, filtered, washed free of salts and dried at 100°C. The dried catalyst was heat treated under flowing $10\%H_2/N_2$ for 1 hour at 650°C to decompose the 1,8-hydroxyquinoline. X-ray diffraction of resulting catalyst showed a single cubic phase with a lattice parameter of 3.91, which indicates little alloying of the components. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was $0.29mgPt/cm^2$.

COMPARATIVE EXAMPLE 6

A catalyst containing Pt and Ru at 38.7 wt%Pt and 20.7 wt%Ru supported on Cabot Vulcan XC72R carbon was prepared as described in Comparative Example 1. X-ray analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.90X, indicating significant alloying of the Ru with the Pt. An electrode containing this catalyst at a platinum loading of $0.29mgPt/cm^2$ was prepared as described in Comparative Example 1.

EXAMPLE 1 - (Pt/Mo/Co)/(Pt/Ru)

A catalyst containing Pt, Mo and Co at 20.30 wt%Pt, 1.44wt%Co and 0.65wt%Mo was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (30.2g) in a solution of sodium hydrogen carbonate (22.3g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 8g Pt) and cobalt dichloride (containing 0.6g Co). After refluxing for 2.5 hrs, the resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was dried at 100°C in air.

The dried catalyst was then re-dispersed in 1 litre of demineralised water for one hour at ambient temperature. To this slurry was added a solution of molybdenum (1.21g) prepared by passing a 1wt% solution of sodium molybdate through an ion exchange column containing Dowex 50-X8 ion exchange resin to covert to colloidal molybdic acid. The combined slurry was then evaporated to dryness. The resulting catalyst was

then heated at 695°C in flowing 5% hydrogen in nitrogen to ensure reduction and alloying of the components. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicating significant alloying of the components

An electrode containing the catalyst at a platinum loading of 0.26mgPt/cm^2 was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.14mgPt/cm^2.

EXAMPLE 2 - (Pt/W/Co)/(Pt/Ru)

A catalyst containing Pt, W and Co at 14.7wt%Pt, 1.0wt%Co and 3.8wt% W was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (32g) in 6 litres of a solution of sodium hydrogen carbonate (18.5g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 5.7g Pt). The resulting slurry was heated under reflux for 2 hrs, before being filtered and washed with demineralised water, until no chloride was detected in the washings. The catalyst was then dried at 100°C in air. The dried catalyst was re-dispersed in 6 litres of sodium hydrogen carbonate (1.1g) solution and heated till under reflux. To this slurry was added a 2wt% solution of cobalt dichloride (containing 0.4g Co). The slurry was then filtered and washed with demineralised water until no chloride was detected in the washings. The wet cake was re-slurried in 1 litre of demineralised water for 1 hr at ambient temperature. To this was

added was added a solution of tungsten (1.5g). The tungsten solution was prepared by dissolving tungsten powder in hydrogen peroxide (100 cm^3 of 28wt% H_2O_2 solution), followed by decomposition of the excess peroxide by platinum black, and subsequent dilution to a 1wt% solution by dimineralised water. The combined slurry was then evaporated to dryness. The resulting catalyst was then heated to 900°C in flowing nitrogen for 1 hour. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.90X indicating significant alloying of the components.

An electrode containing this catalyst at a platinum loading of 0.27mgPt/cm^2 was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of a catalyst containing Pt and Ru at 37.1 wt%Pt and 17.9 wt%Ru supported on Cabot Vulcan XC72R carbon was prepared as described in Comparative Example 1, was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.24 mgPt/cm^2. X-ray analysis of this catalyst showed a single cubic phase with a lattice parameter of 3.90X, indicating significant alloying of the Ru with the Pt. An electrode containing this catalyst at a platinum loading of 0.29mgPt/cm^2 was prepared as described in Comparative Example 1.

EXAMPLE 3 - (Pt/Ru/W)/(Pt/Ru)

A catalyst containing Pt, Ru and W was prepared as described in Comparative Example 2. An electrode containing this catalyst at a platinum loading of 0.12mgPt/cm^2 was

prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst as used in Example 2 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.25mgPt/cm^2.

EXAMPLE 4 - (Pt/Ti/W)/(Pt/Ru)

A catalyst containing Pt, Ti and W was prepared as described in Comparative Example 4. An electrode containing this catalyst at a platinum loading of 0.16mgPt/cm^2 was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 2 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.13mgPt/cm^2.

EXAMPLE 5 – (PtMoCo)/(PtRu)

A catalyst containing Pt, Co and Mo was prepared as described in Comparative Example 5. An electrode containing this catalyst at a platinum loading of 0.15mgPt/cm^{-2} was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 6 was applied using the method described in Comparative Example 1. The addition loading in this catalyst layer was 0.31 mgPtcm^{-2}.

TABLE 1

Example Number	Catalyst	Assay Characterisation Data /wt% of total catalyst weight			Atomic Ratio	XRD Characterisation	
		Pt	2nd Metal	3rd Metal		Crystallite Size /nm	Pt lattice parameter /X
Comp. 1	PtRu	41.80	20.78		51:49	2.6	3.87
Comp. 2	PtRu	19.2	9.3		52:48	1.9	3.88
Comp. 3	PtRuW	16.65	8.32	10.77	38:36:26	4.6	3.87
Comp. 4	PtTiW	34.41	2.02	10.63	64:15:21	5.6	3.93
Comp. 5	PtCoMo	21.9	0.2	1.0	89:03:08	4.5	3.91
Comp. 6	PtRu	38.7	20.7		49:51	2.7	3.90
1	PtCoMo	20.30	1.44	0.65	77:18:05	4.2	3.87
	PtRu	41.80	20.78		51:49	2.6	3.87
2	PtCoW	14.7	1.0	3.76	67:15:18	3.1	3.90
	PtRu	19.2	9.3		52:48	1.9	3.88
3	PtRuW	16.65	8.32	10.77	38:36:26	4.6	3.87
	PtRu	37.06	17.89		52:48	3.2	3.90
4	PtTiW	34.41	2.02	10.63	64:15:21	5.6	3.93
	PtRu	19.2	9.3		52:48	1.9	3.88
5	PtCoMo	21.9	0.2	1.0	89:03:08	4.5	3.91
	PtRu	38.7	20.7		49:51	2.7	3.90

EXAMPLE 6-PREPARATION OF MEAs

The electrode structures of the invention were first produced as anodes and then bonded to membranes to form MEAs. as described in Example 2 of EP 731 520. The MEA was

fabricated by hot-pressing the anode and a pure platinum catalyst cathode (with a platinum loading of 0.6mg Pt/cm^2) against each face of a solid proton-conducting electrolyte membrane. The membrane used was the perfluorinated membrane Nafion® 115 (from Du Pont de Nemours). MEAs of 6.5 cm^2 area were formed by hot-pressing at pressures of 100 psi (1 psi = 6.89 x 10^3 N/m^2) over the MEA, at temperatures exceeding the glass transition temperature of the membrane, as is commonly practised in the art. MEAs of 240 cm^2 area were formed by hot pressing at pressures of 400 psi over the MEA.

EXAMPLE 7-PERFORMANCE EVALUATION

The MEAs were evaluated in a PEMFC single cell. The single cell consists of graphite plates into which flowfields are machined to distribute the reactant gases, humidification water and heating and cooling water and to remove products. The MEA was located between the appropriate flowfield plates. The cell is compressed, typically to a gauge pressure of 70 psig above the reactant gas pressure.

The "fuel cell performance" was assessed by measuring the voltage at a fixed current density of 500 mA cm^{-2}. The fuel cell operated under conditions representative of those employed in practical PEM fuel cells. These conditions were typically a reactant gas inlet temperature of 80°C, a pressure of both hydrogen and air reactants of 3 atmospheres. For 6.45 cm^2 MEAs, the reactant gas streams were kept constant at 0.1SLPM (standard litres at 1 bar and 0°C per minute); 0.125 SLPM for 25% CO_2 and 75% hydrogen; and 0.4 SLPM for oxygen. For 240 cm^2 MEAs, the fuel to air gas stoichiometry was 1.5/2. For the single cell reformate tolerance experiments, the anode

gas stream was changed at time t=0 from pure hydrogen to gas streams composed of 100ppm CO in hydrogen, 25% CO_2 in hydrogen, 40ppm CO and 25% CO_2 in hydrogen or 100ppm CO and 25% CO_2 in hydrogen. The fuel cell performance using the binary gas mixtures was performed using the 6.45 cm^2 MEAs, while testing using the ternary gas mixtures was performed using the 240 cm^2 MEAs. At constant current density of 0.5 Acm^{-2}, the cell potential was then monitored with time in order to assess the CO and the CO_2 tolerance of different catalysts under practical conditions. Table 2 summarises the CO, CO_2 and CO/CO_2 tolerances of the catalysts described in the Examples in the form of voltage losses (in mV) on the different poisoning gas streams, when compared to operation on pure hydrogen. The lower the voltage loss, the more resistant the catalyst or catalyst combination is towards being poisoned on that particular gas stream.

Figure 1 shows fuel cell performance data of cell voltage vs time for operation of two PtRu, PtRuW, PtTiW and PtCoMo catalysts in a gas stream containing 100ppm CO in hydrogen. The anode platinum loadings are respectively 0.37, 0.25, 0.29, 0.45 and 0.29 mg Pt/cm^2. Figure 1 shows that the single cell voltages for all five MEAs decay from their value at t=0 min when the cell is operated with pure hydrogen. Figure 1 shows that the performance curves of the two MEAs containing PtRu anode catalysts, one labelled "standard" PtRu and the other labelled "advanced" PtRu. This represents the range of CO tolerance performance found with state of the art PtRu catalysts as a function of Pt loading on the carbon and Pt loading in the catalyst layer. The MEA containing the advanced PtRu catalyst, shows the lowest drop in performance on switching between pure hydrogen and 100ppm CO in hydrogen. This catalyst has a higher Pt loading on carbon and a higher loading of catalyst in the electrode compared to the standard PtRu

catalyst. The electrode containing the advanced PtRu catalyst would be expected to give a higher performance due to the higher density of Pt in the catalyst layer. The performance curves of the MEA's containing the three ternary catalysts, PtRuW, PtTiW and PtCoMo on 100ppm CO in hydrogen show them lying between the two PtRu performance curves, indicating comparable CO tolerance. Considering that the dispersion of the catalyst particles as shown in Table 1 as Pt crystallite size, are significantly inferior to those displayed by the two PtRu catalysts, then these catalysts are intrinsically more CO tolerant than state of the art PtRu catalysts, in terms of specific activity (ie activity per actual surface area of Pt present).

Figure 2 shows fuel cell performance data of cell voltage *vs* time for operation of the two PtRu, PtRuW, PtTiW and PtCoMo catalysts in a gas stream containing 25% CO_2 and 75% hydrogen. The anode platinum loadings are the same as in Figure 1. Figure 2 shows that the single cell voltages for al five MEAs decay from their value at t=0 min when the cell is operated with pure hydrogen. The performances of the electrodes containing the PtRu catalysts degrades by 19 and 38 mV respectively, on the introduction of the gas mixture containing 25% CO_2 and 75% hydrogen. In contrast, the performance of the electrodes containing the three ternary catalysts degrade by larger amounts, with the PtCoMo catalyst losing 211 mV on introduction of the CO_2/H_2 gas mixture. This shows that although the ternary catalysts have good CO tolerance, they have inferior CO_2 tolerance to the 'state-of-the-art' PtRu catalysts.

Figure 3 presents single cell performance data for electrode bilayers according to the invention operating in 25% CO_2 and 75% hydrogen. The bilayers comprise of catalyst

layers of PtTiW, PtRuW, PtCoMo and PtCoW containing 0.16, 0.12, 0.26 and 0.27 mg Pt cm^{-2} and layers of PtRu catalyst at loadings of 0.13, 0.25, 0.14 and 0.24 mg Pt cm^{-2}, respectively. Figure 3 also shows the comparative example PtRu which is also presented in Figure 1. The bilayer electrodes according to the invention show small decays when the gas stream is changed at t=0 min from pure hydrogen to 25%CO_2 and 75% hydrogen. The performance decay of the PtRuW catalyst when as a bilayer with PtRu shows a significant reduction. The other electrode samples exhibit a decay around 25 mV, very close to the comparative PtRu electrode. Therefore, the combination of Pt ternary catalysts with PtRu catalysts, has overcome the CO_2 "in-tolerance" of these catalyst seen, when tested as single catalyst layers.

Figure 4 shows that, at the same time, the performance of the bilayer electrodes of the invention in hydrogen containing 100 ppm CO is significantly improved over the comparative PtRu sample. When at t=0 min the gas stream is changed from pure hydrogen to hydrogen containing 100 ppm CO, all samples exhibit, after some induction time, a decay of the single cell voltage. This decay is 166 mV for the comparative PtRu sample. All bilayer samples show lower performance decay, while the total platinum loading in both layers is very similar in all cases. The PtCoMo/PtRu bilayer electrode of the invention shows a performance decay as low as approximately 88 mV. In addition, the PtCoW/PtRu bilayer electrode of the invention shows a performance decay of 73 mV, although with a higher overall electrode loading of 0.51 mg Pt/cm^2.

Figure 5 shows the single cell performances of two MEA's, one an electrode bilayer

according to the invention, and the other a single catalyst layer, operating on gas mixtures of CO and CO_2 in hydrogen, which has been used to simulate reformate gas compositions. The MEA's have been tested on two different gas mixtures; 40ppm CO and 25% CO_2 in hydrogen, and 100ppm CO and 25% CO_2 in hydrogen. The bilayer comprises of a catalyst layer of PtCoMo at loadings of 0.15 mg Pt/cm^2 and a layer of a PtRu catalyst at a loading of 0.31 mg Pt/cm^2. The single layer electrode comprised of the same PtRu catalyst at a loading of 0.29 mg Pt/cm^2. Figure 5 shows that the performance of the bilayer electrode is superior to the single layer with both the gas mixtures tested. In particular, the differences between the two electrodes is increased with the gas mixture with 100ppm CO.

Clearly, the bilayer electrode according to the invention shows improved performance when tested in gas streams of CO in hydrogen, CO_2 in hydrogen and mixtures of CO and CO_2 in hydrogen, when compared to single layer electrodes of similar Pt loading. In particular, the combination of two different catalysts within the bilayer electrode have shown unexpectedly improved performances based on their performances as single layers.

TABLE 2

Example	Catalyst(s)	Pt loading /mgPtcm^{-2}	Voltage Losses on Different Poisoning Gas Streams /mV			
			100ppmCO /H_2	25%CO2/H_2	40ppmCO/ 25%CO_2/H_2	100ppmCO/ 25%CO_2/H_2
Comp. 1	PtRu	0.37	166	19	-	-
Comp. 2	PtRu	0.25	325	38	-	-

Comp. 3	PtRuW	0.29	177	56	-	-
Comp. 4	PtTiW	0.45	195	51	-	-
Comp. 5	PtCoMo	0.29	274	211	-	-
Comp. 6	PtRu	0.29	-	-	114	173
1	PtCoMo/PtRu	0.26/0.14	88	29	-	-
2	PtCoW/PtRu	0.27/0.24	73	22	-	-
3	PtRuW/PtRu	0.12/0.25	110	44	-	-
4	PtTiW/PtRu	0.16/0.13	165	29	-	-
5	PtCoMo/PtRu	0.15/0.31	-	-	61	83

CLAIMS

1. An electrode structure comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum.

2. An electrode structure according to claim 1, wherein the one or more metals(s) X or M is or are selected from the groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press.

3. An electrode structure according to claim 1 or claim 2, wherein X is selected from Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; especially Ru, Mn, Co, Ni Rh and Ni.

4. An electrode structure according to claim 1 or claim 2, wherein M is selected from Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; especially Ru or Rh.

5. An electrode structure according to any preceding claim, wherein Y is selected from one or more of the Group IVB to VIB elements and rhenium, or an oxide thereof.

6. An electrode structure according to any preceding claim, wherein Y is Ti, V, Nb, Ta, Mo, W, Re, or an oxide thereof; such as Ti, V, Ta, Mo, W, or an oxide thereof.

7. An electrode structure according to any preceding claim, wherein Y is Mo or W; or an oxide thereof, such as WO_3 or MoO_3.

8. An electrode structure according to claim 1, wherein the first catalytic component is selected from: Pt/Mo, Pt/Ru, Pt/Mo/Co, Pt/W/Co, Pt/Ru/WO_3 and Pt/Ti/W; and the second catalytic component is Pt/Ru.

9. An electrode comprising an electrode structure according to any preceding claim wherein the electrocatalyst materials are present on one side of a gas diffusion material.

10. A catalysed membrane comprising an electrode structure according to any one or more of claims 1 to 8 wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material.

11. An MEA comprising an electrode structure according to any one or more of claims 1 to 8.

12. An electrode according to claim 9, a catalysed membrane according to claim 10 or an MEA according to claim 11 wherein the two catalyst materials are formulated into two separate layers.

13. An electrode according to claim 9, a catalysed membrane according to claim 10 or an MEA according to claim 11 wherein the two catalyst materials are formulated into one mixed layer.

14. A fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M where M is a metal alloyed with the platinum.

15. Use of an electrode structure according to any one or more of claims 1 to 8 in a fuel cell.

16.An electrode, such as an anode, such as a fuel cell anode; an electrochemical device, such as an MEA; a use; or a method, substantially as hereinbefore described with particular reference to the examples.

FIGURE 1

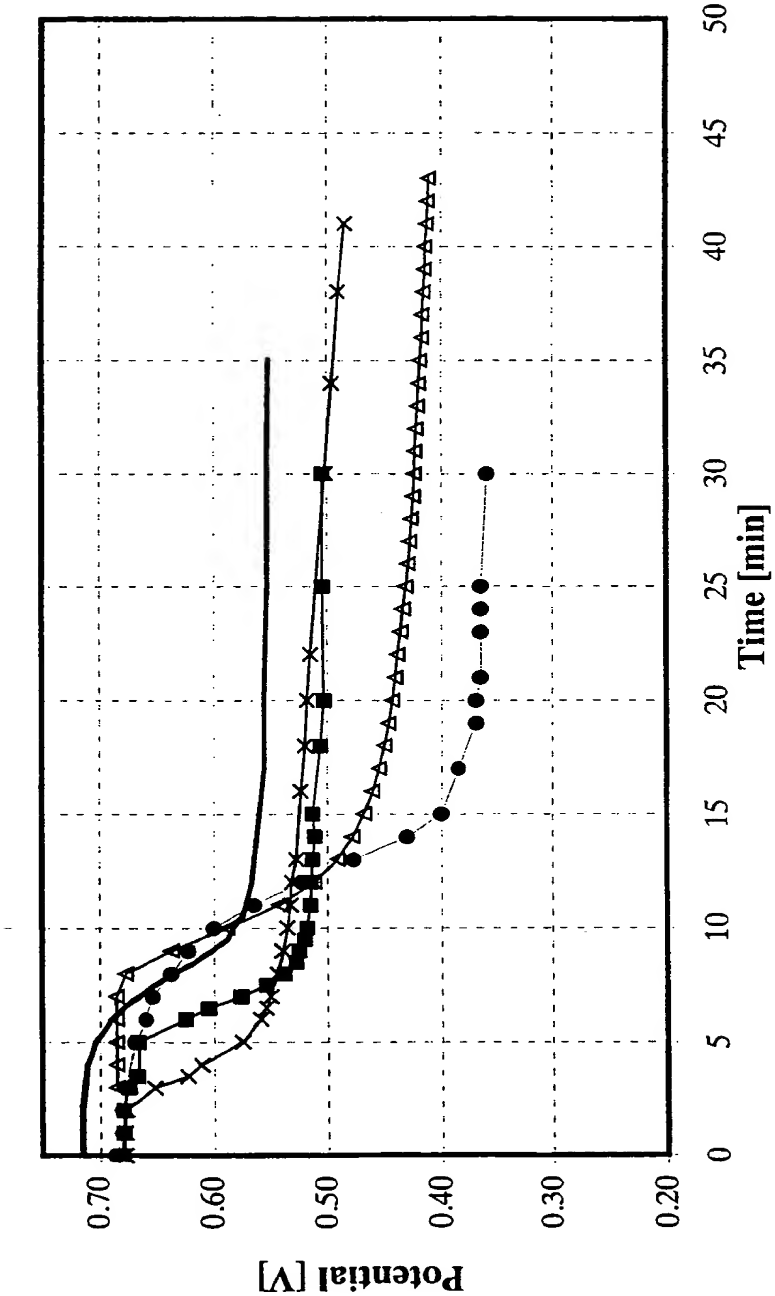
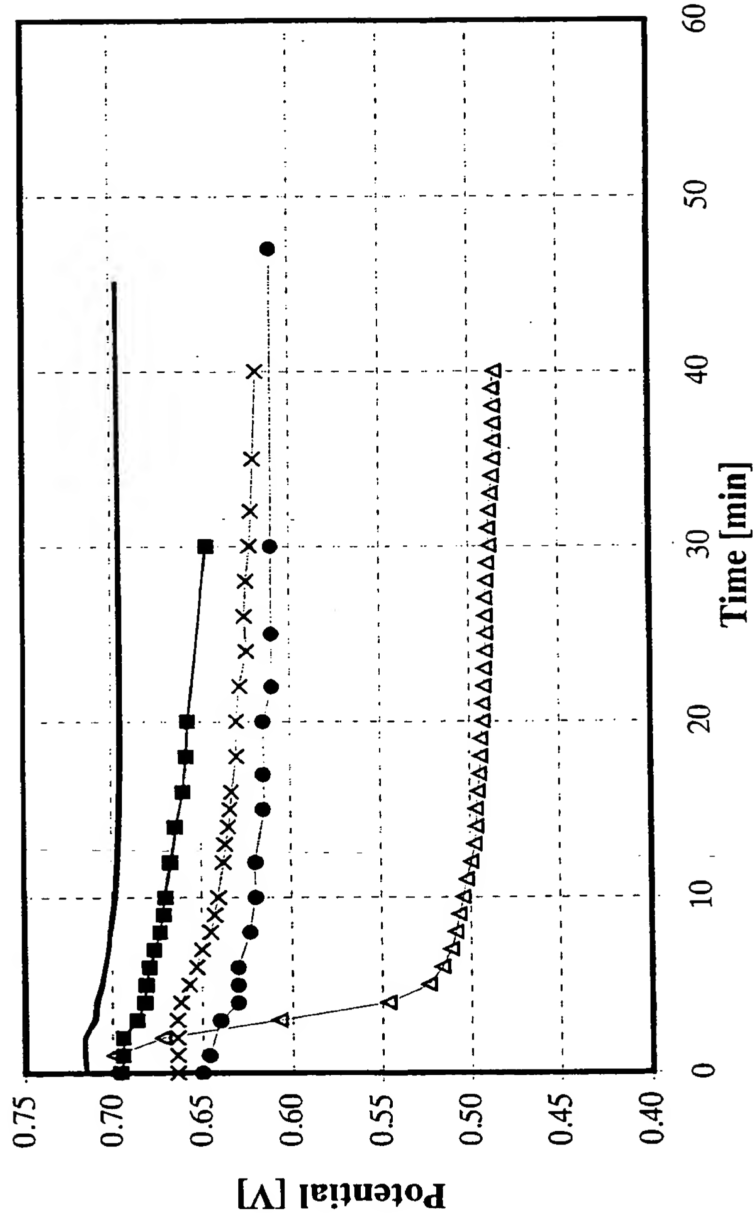

Potential [V]
0.70
0.60
0.50
0.40
0.30
0.20
Time [min]
0
5
10
15
20
25
30
35
40
45
50

FIGURE 2


Potential [V]
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0.70
0.65
0.60
0.55
0.50
0.45
0.40
Time [min]
0
10
20
30
40
50
60

FIGURE 3

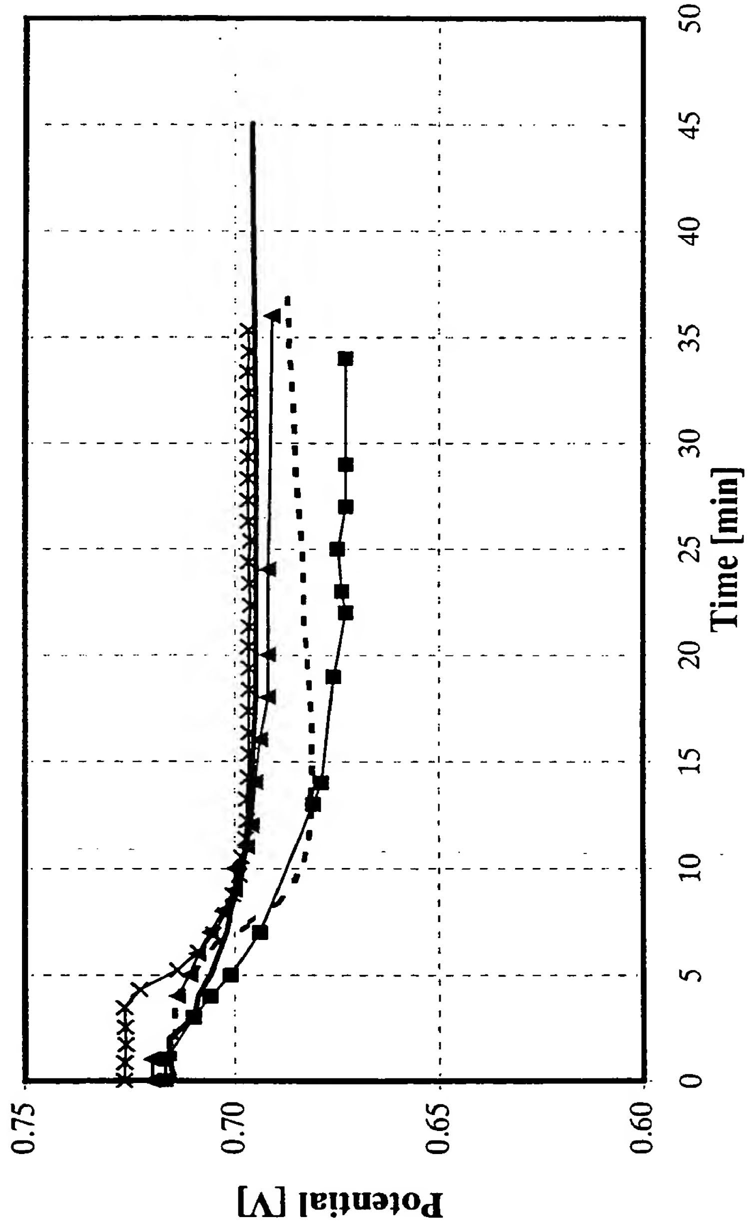


FIGURE 4

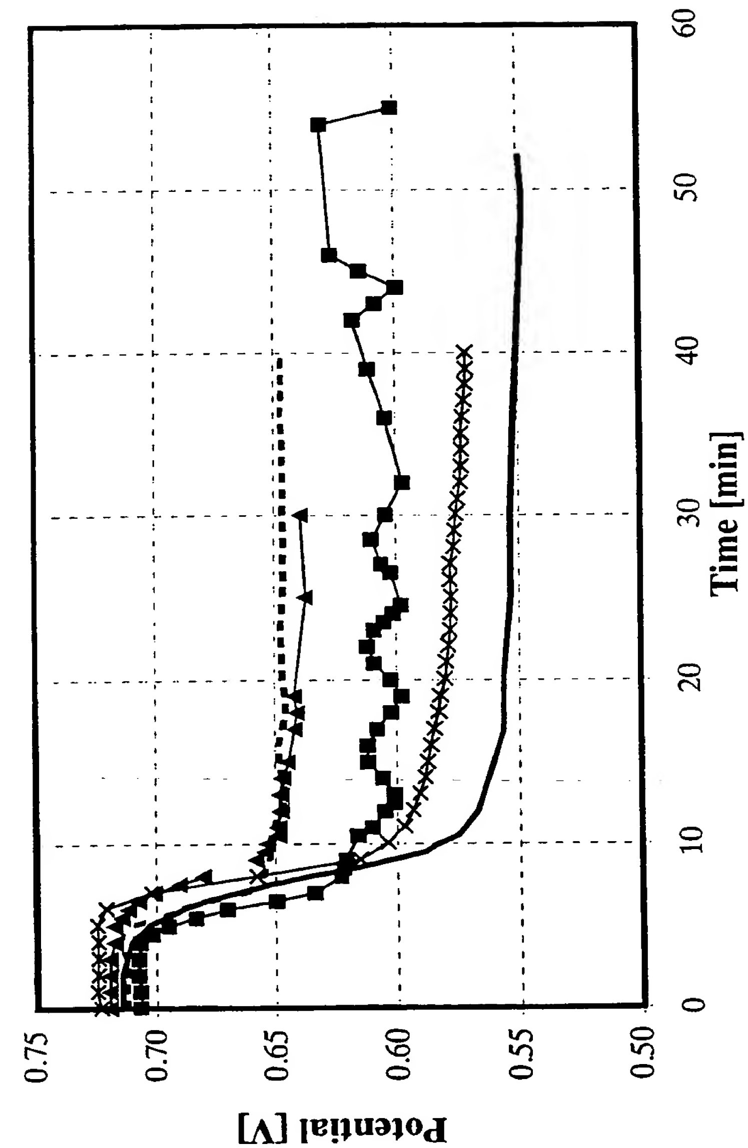
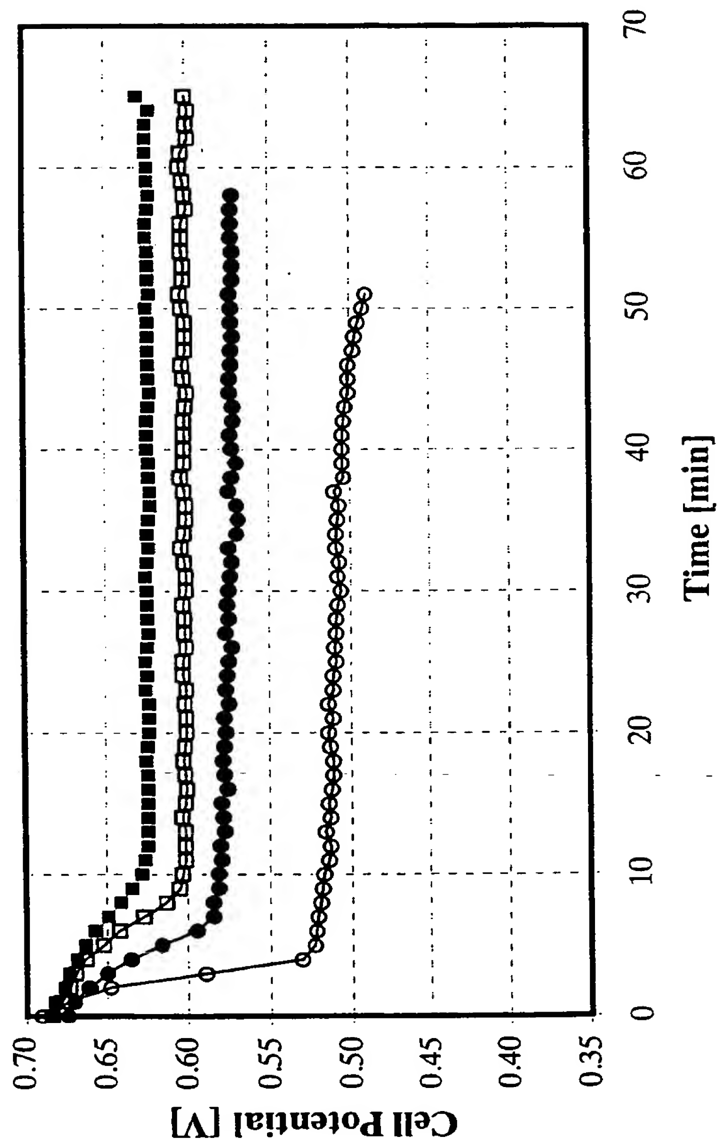


FIGURE 5


Cell Potential [V]
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
Time [min]
0
10
20
30
40
50
60
70

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04081

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/92 H01M8/10 B01J23/40 B01J23/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M B01J C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 736 921 A (BALLARD POWER SYSTEMS ;JOHNSON MATTHEY PLC (GB)) 9 October 1996 (1996-10-09) column 5, line 15 - line 34 column 6, line 55 -column 7, line 32 column 8, line 41 -column 9, line 1 claims 1,5-9,11-15 ---	1-16
Y	EP 0 838 872 A (JOHNSON MATTHEY PLC) 29 April 1998 (1998-04-29) cited in the application page 3, line 30 - line 36 page 3, line 46 -page 4, line 27 examples 1,2; table 1 page 6, line 52 - line 58 claims 1-17 ---	1-16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 March 2000	29/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Gamez, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GOTZ M ET AL: "Binary and ternary anode catalyst formulations including the elements W, Sn and Mo for PEMFCs operated on methanol or reformate gas" ELECTROCHIMICA ACTA,GB,ELSEVIER SCIENCE PUBLISHERS, BARKING, vol. 43, no. 24, 21 August 1998 (1998-08-21), pages 3637-3644, XP004132402 ISSN: 0013-4686 page 3637, left-hand column, paragraph 1 -right-hand column, paragraph 1 page 3638, left-hand column, paragraph 3 -right-hand column, paragraph 2 tables 1,2 page 3640, left-hand column, paragraph 2 - paragraph 3	1-3,5-9, 11,14-16
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 511 (E-1432), 14 September 1993 (1993-09-14) & JP 05 135772 A (FUJI ELECTRIC CO LTD), 1 June 1993 (1993-06-01) abstract -& DATABASE WPI Section Ch, Week 199326 Derwent Publications Ltd., London, GB; Class L03, AN 1993-209759 XP002133323 & JP 05 135772 A (FUJI ELECTRIC MFG CO LTD), 1 June 1993 (1993-06-01) abstract	1-3,5-9, 14-16
A	A ET AL: "Precious metal/hydrogen bronze anode catalysts for the oxidation of small organic molecules and impure hydrogen" JOURNAL OF POWER SOURCES,CH,ELSEVIER SEQUOIA S.A. LAUSANNE, vol. 61, no. 1-2, 8 July 1996 (1996-07-08), pages 223-225, XP004071514 ISSN: 0378-7753 page 223, right-hand column, paragraph 1 - paragraph 2 page 224, left-hand column, paragraph 4 -right-hand column, paragraph 3 table 1	1-3,5-8, 14-16

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04081

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	L. W. NIEDRACH AND I. B. WEINSTOCK: "Performance or carbon monoxide in Low-temperature fuel cells containing oxide catalysts" ELECTROCHEMICAL TECHNOLOGY, vol. 3, no. 9-10, September 1965 (1965-09), page 270-275 XP002133322 cited in the application page 270, left-hand column, paragraph 2 table 1 page 271, right-hand column, paragraph 3 table 2 page 273, line R, paragraph 4 -page 274, line R, paragraph 1	1,5-8, 14-16

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/04081

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0736921	A	09-10-1996	AU	5048596	A	17-10-1996
			CA	2173563	A	06-10-1996
			DE	69600422	D	20-08-1998
			DE	69600422	T	10-12-1998
			JP	9027326	A	28-01-1997
			US	5795669	A	18-08-1998
EP 0838872	A	29-04-1998	JP	10228912	A	25-08-1998
			US	5939220	A	17-08-1999
JP 05135772	A	01-06-1993	NONE			

CLAIMS

1. An electrode structure comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum.

2. An electrode structure according to claim 1, wherein the one or more metals(s) X or M is or are selected from the groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press.

3. An electrode structure according to claim 1 or claim 2, wherein X is selected from Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; especially Ru, Mn, Co, Ni Rh and Ni.

4. An electrode structure according to claim 1 or claim 2, wherein M is selected from Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; especially Ru or Rh.

5. An electrode structure according to any preceding claim, wherein Y is selected from one or more of the Group IVB to VIB elements and rhenium, or an oxide thereof.

6. An electrode structure according to any preceding claim, wherein Y is Ti, V, Nb, Ta, Mo, W, Re, or an oxide thereof; such as Ti, V, Ta, Mo, W, or an oxide thereof.

7. An electrode structure according to any preceding claim, wherein Y is Mo or W; or an oxide thereof, such as WO_3 or MoO_3.

8. An electrode structure according to claim 1, wherein the first catalytic component is selected from: Pt/Mo, Pt/Ru, Pt/Mo/Co, Pt/W/Co, Pt/Ru/WO_3 and Pt/Ti/W; and the second catalytic component is Pt/Ru.

9. An electrode comprising an electrode structure according to any preceding claim wherein the electrocatalyst materials are present on one side of a gas diffusion material.

10. A catalysed membrane comprising an electrode structure according to any one or more of claims 1 to 8 wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material.

11. An MEA comprising an electrode structure according to any one or more of claims 1 to 8.

12. An electrode according to claim 9, a catalysed membrane according to claim 10 or an MEA according to claim 11 wherein the two catalyst materials are formulated into two separate layers.

13. An electrode according to claim 9, a catalysed membrane according to claim 10 or an MEA according to claim 11 wherein the two catalyst materials are formulated into one mixed layer.

14. A fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M where M is a metal alloyed with the platinum.

15. Use of an electrode structure according to any one or more of claims 1 to 8 in a fuel cell.

16. An electrode, such as an anode, such as a fuel cell anode; an electrochemical device, such as an MEA; a use; or a method, substantially as hereinbefore described with particular reference to the examples.